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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08G 18/62, B05D 1/36</b> <b>C09D 133/14</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/00380</b> <b>(43) International Publication Date:</b> 7 January 1993 (07.01.93)
<b>(21) International Application Number:</b> PCT/US92/04194 <b>(22) International Filing Date:</b> 27 May 1992 (27.05.92)  <b>(30) Priority data:</b> 718,541 20 June 1991 (20.06.91) US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventor:</b> HARPER, Lee, R. ; 330 South Middletown Road, Media, PA 19063 (US).  <b>(74) Agents:</b> FRICKE, Hilmar, L. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> BR, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> LOW VOLATILE ORGANIC CONTENT COATING COMPOSITION FOR BASECOAT/CLEAR COAT FINISH  <b>(57) Abstract</b>  An improved process for forming multiple coats of finishes on a substrate by sequential (a) applying to the substrate a layer of a color basecoat composition of waterborne coating composition of an acrylic polymer latex contains pigment; (b) applying to the layer of color basecoat composition before it is fully cured a clear coat composition of an acrylic polymer having crosslinkable groups and a crosslinking agent in a volatile organic solvent and (c) subsequently simultaneously curing the basecoat composition and the clear coat composition; the improvement used therewith comprises a solvent based clear coating composition having a binder of about 40-95 % by weight of an acrylic polymer having at least two alkyl methacrylates having 2-12 carbon atoms in the alkyl group, a hydroxy alkyl methacrylate having 2-4 carbon atoms in the alkyl group and having a weight average molecular weight of about 3,000-10,000 and a glass transition temperature of about -20 to + 50 °C; and 5-60 % by weight an organic polyisocyanate; wherein the clear coat when cured has a water vapor permeability value of about 1400-3200.		

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Title

LOW VOLATILE ORGANIC CONTENT COATING COMPOSITION FOR  
BASECOAT/CLEAR COAT FINISH

5                   BACKGROUND OF THE INVENTION

This invention is directed to an improved process for applying a low VOC (volatile organic content) solvent based clear coating composition over a waterborne base coating to form a clear coat/basecoat  
10   finish of automotive quality and appearance.

Waterborne coating compositions useful for basecoats for automotive applications are shown in Den Hartog et al US 4,954,559 issued September 4,1990. The application of a clear coat to a basecoat in a "wet  
15   on wet" application is shown in Kurauchi et al US 4,728,543 issued March 1, 1988 and Benefiel et al US 3,639,147 issued February 1, 1972. However, none of the compositions or processes shown in the art form a clear coat/basecoat finish wherein the clear coat is formed  
20   from a solvent based composition and the color coat is formed from a waterborne composition and wherein the finish has properties that are required for exterior finishes of automobiles and trucks and the compositions meet desired standards of overall low solvent emissions.

25               One problem in particular that has been encountered with clear coat/basecoat finishes is the degradation and delamination of the clear coat from a waterborne basecoat upon weathering. Moisture penetration of the clear coat is believed to cause at  
30   least a part of the aforementioned problem. The novel process of this invention which uses a particular clear coat forms a clear coat/basecoat finish of automotive quality that is weatherable and durable and the process meets current standards of solvent emissions.

SUMMARY OF THE INVENTION

An improved process for forming multiple coats of finishes such as a basecoat/clear coat finish on a substrate using the following sequential steps of

5 (a) applying to the substrate a color basecoat composition of a waterborne basecoat having a film forming binder of an acrylic polymer latex and contains pigment in a pigment to binder ratio of about 1:100 to 150:100 dispersed in an aqueous medium; (b) applying to

10 the layer of the color basecoat composition before the basecoat composition is fully cured, a clear coat composition of an acrylic polymer having crosslinkable groups and a crosslinking agent in a volatile organic solvent and (C) subsequently simultaneously curing the

15 basecoat composition and the clear coat composition; the improvement that is used with this process is a clear coating composition that contains about 40-80% by weight, based on the weight of the coating composition, of a binder and correspondingly, about 20-60% by weight

20 of a volatile organic solvent; wherein the binder contains about

40-95% by weight, based on the weight of the binder, of an acrylic polymer of polymerized monomers of at least two alkyl methacrylates

25 having about 2-12 carbon atoms in the alkyl group and a hydroxy alkyl methacrylate having 2-4 carbon atoms in the alkyl group and the polymer having a weight average molecular weight of about 3,000-10,000 and a glass

30 transition temperature of about -20 to +50°C; and

5-65% by weight, based on the weight of the binder, of an organic polyisocyanate crosslinking agent and

wherein a cured layer of the clear coat has a water permeability value of about 1400-3200.

Another aspect of this invention is an article coated by the above process.

5

#### DETAILED DESCRIPTION OF THE INVENTION

Weight average molecular weight is determined by gel permeation chromatography using polymethyl methacrylate as the standard.

10 Glass transition temperature is determined by differential scanning calorimetry.

Water permeability is determined by the procedure described in Yasuda, H. and Stennett, V., Journal of Polymer Science, Vol. 57, p 907 (1962). The  
15 water vapor permeability value is expressed as cc. water vapor at STP/cm.<sup>2</sup> of film/cm. film thickness/sec./cm.Hg.

The term "latex" as used herein means a dispersion in an aqueous carrier of polymer particles having a particle size of about 0.06-0.20 microns and a  
20 weight average molecular weight of greater than 500,000.

The term "hydrosol" as used herein means a fine dispersion in an aqueous carrier of polymer particles having a particle size of less than 0.30 microns, preferably less than 0.15 microns and more  
25 preferably less than 0.01 microns and a weight average molecular weight of less than 100,000.

The clear coating composition used in the process of this invention has a low VOC (volatile organic content) and forms a finish that is hard,  
30 glossy, weatherable and durable. In particular, the composition has excellent adhesion to a coating of a waterborne acrylic polymer and to a variety of other substrates such as previously painted substrates, cold rolled steel, phosphatized steel, steel coated with  
35 conventional primers such as electrodeposition primers

that typically are crosslinked epoxy polyesters and various epoxy resin, alkyd resin repair primers, plastic substrates such as polyester reinforced fiber glass, reaction injection molded urethanes and partially  
5 crystalline polyamides.

The clear coating composition has a film forming binder content of about 40-80% by weight and correspondingly, about 20-60% by weight of a volatile organic solvent or blend of solvents for the binder. The  
10 composition may contain very small amounts of pigment to eliminate color such as yellowing and may contain transparent pigments having the same or similar refractive index as the binder to improve weatherability and durability of the resulting clear coat. Typically  
15 useful pigments have a particle size of about 0.015-50 microns and are used in a pigment to binder weight ratio of about 1:100 to 10:100 and are for example inorganic siliceous pigments such as silica pigments having a refractive index of about 1.4-1.6.

The film forming binder of the clear coating composition contains about 40-95% by weight of an acrylic polymer and about 5-60% by weight of an organic polyisocyanate crosslinking agent. The acrylic polymer is of polymerized monomers of at least two alkyl  
25 methacrylates having 2-12 carbon atoms in the alkyl group and hydroxy alkyl methacrylate having 2-4 carbon atoms in the alkyl group. The polymer has a weight average molecular weight of about 3,000-10,000, preferably 3,000-8,000 and a glass transition  
30 temperature of about -20 to +50°C, preferably 0-35°C. Preferably, the polymer contains about 70-90% by weight of at least two alkyl methacrylates and 10-30% by weight of a hydroxy alkyl methacrylate.

Typically useful alkyl methacrylates are  
35 ethyl methacrylate, propyl methacrylate, isopropyl

methacrylate, butyl methacrylate, isobutyl methacrylate, pentyl methacrylate, hexyl methacrylate, 2-ethyl hexyl methacrylate, nonyl methacrylate, lauryl methacrylate and the like.

5 Typically useful hydroxy alkyl methacrylates are hydroxy ethyl methacrylate, hydroxy propyl methacrylate, hydroxy butyl methacrylate and the like.

The acrylic polymer also may contain about 0.5-40% by weight of polymerized styrene monomer.

10 One preferred polymer contains about 20-40% by weight of isobutyl methacrylate, 35-65% by weight of 2-ethylhexyl methacrylate and 15-30% by weight of 2-hydroxy ethyl methacrylate.

15 Water vapor permeability of a finish can be reduced by using acrylic polymers formed with monomers having bulky side chains such as isobutyl methacrylate and 2-ethyl hexyl methacrylate

20 The acrylic polymer for the clear coat is prepared by a conventional solution polymerization process in which the monomers, solvents and polymerization catalyst are heated to about 140-160°C for about 2-4 hours to form the polymers.

25 Typical polymerization catalyst are azo type catalyst such as azo-bis-isobutyronitrile, acetate catalyst such as t-butyl peracetate, di-t-butyl peroxide, t-butyl perbenzoate, t-butyl peroctoate and the like.

30 Typical solvents that can be used are ketones such as methyl amyl ketone, isobutyl ketone, methyl ethyl ketone, aromatic hydrocarbons such as toluene, xylene, alkylene carbonates such as propylene carbonate, n-methyl pyrrolidone, ethers, esters, acetates and mixtures of any of the above.

35 The organic polyisocyanate crosslinking agent can be any of the conventional aromatic, aliphatic,



cycloaliphatic diisocyanates, trifunctional isocyanate, and isocyanate functional adducts of a polyol and a diisocyanate. Typical diisocyanates that can be used are for example 1,6-hexamethylene diisocyanate, isophorone  
5 diisocyanate, 4,4'-biphenylene diisocyanate, toluene diisocyanate, bis cyclohexyl diisocyanate, tetramethyl xylene diisocyanate, ethylethylene diisocyanate, 2,3-dimethyl ethylene diisocyanate, 1-methyltrimethylene diisocyanate, 1,3-cyclopentylene diisocyanate,  
10 1,4-cyclohexylene diisocyanate, 1,3-phenylene diisocyanate, 1,5-naphthalene diisocyanate, bis-(4-isocyanatocyclohexyl)-methane, 4,4'-diisocyanatodiphenyl ether and the like.

Typical trifunctional isocyanates that can be  
15 used are triphenylmethane triisocyanate, 1,3,5-benzene triisocyanate, 2,4,6-toluene triisocyanate and the like. Trimers of diisocyanates can also be used such as the trimer of hexamethylene diisocyanate which is sold under the tradename "Desmodur" N-3390.

20 Isocyanate functional adducts can be used that are formed from an organic polyisocyanate and a polyol. Any of the aforementioned polyisocyanates can be used with a polyol to form such adducts. Polyols such as trimethylol alkanes like trimethylol propane or ethane  
25 can be used. One preferred adduct is formed from tetramethylxylidene diisocyanate and trimethylol propane and is sold under the tradename "Cythane" 3160.

To improve weatherability of the composition, about .01-10% by weight of ultraviolet light  
30 stabilizers, screeners, quenchers and antioxidants can be added. Typical ultraviolet light screeners include benzophenones, benzoates, triazines, triazoles, hindered amines and any mixtures thereof. Typical useful hindered amine ultraviolet light stabilizers are  
35 bis(1,2,2,5,6 pentamethyl-4-piperidiny)l sebacate),

di[4(2,2,6,6 tetramethyl piperidiny)] sebacate and the like.

One typically useful aqueous basecoating composition has a film forming binder of about 60-90% by weight of a methylol (meth)acrylamide acrylic latex and about 10-40% by weight of an acrylic hydrosol polymer. This composition can be cured at ambient temperatures.

The latex and hydrosol polymers each contain methylol (meth)acrylamide and form an aqueous polymer system which cures at ambient temperatures to form a crosslinked finish having excellent adhesion, water resistance, solvent resistance, hardness, durability and weatherability as is required for an automotive or a truck finish. The hydrosol polymer preferably contains the same or similar monomers as the latex polymer and is compatible with the latex polymer and readily crosslinks on curing. In particular, the latex polymer and the hydrosol polymer contain the same or very similar amounts of carboxyl and hydroxyl monomers which improves the humidity performance of finishes formed from coatings containing such polymers.

Because the hydrosol polymer is relatively low in molecular weight in comparison to the latex polymer, it is more mobile than the latex polymer particles and fills the voids formed by the latex polymer particles upon drying. This substantially improves the physical properties of the resulting film or finish.

The methylol (meth)acrylamide of the latex and hydrosol polymers reacts with itself or with another hydroxy group thereby forming a crosslinked film or finish.

The acrylic latex polymer is formed by conventional emulsion polymerization by emulsifying a mixture of monomers, water, surfactant and

polymerization catalyst and charging the resulting emulsion into a conventional polymerization reactor and heating the constituents in the reactor to about 60-95°C for about 15 minutes to 8 hours and then the resulting polymer is neutralized with ammonia or an amine. The size of the polymeric particles of the latex is about 0.06-0.20 microns. The resulting polymer has a hydroxyl no. of 2-100, a glass transition temperature of -40 to +40°C and a weight average molecular weight of about 500,000 - 3,000,000.

The acrylic latex polymer used in the basecoat contains about 1-15% by weight of polymerized methylol methacrylamide, methylol acrylamide or any mixtures thereof.

The acrylic latex polymer preferably contains sufficient polymerized hydroxy alkyl methacrylate or acrylate having 2-4 carbon atoms in the alkyl group to provide the polymer with a hydroxyl no. of 2-100. Usually, about 0.5-10% by weight of hydroxy alkyl acrylate or methacrylate is used. Other useful polymerizable constituents are reaction products of an alkyl methacrylate or acrylate and a lactone. A constituent of this type is "Tone" 100 made by Union Carbide which is believed to be the reaction product of hydroxyethyl acrylate and a lactone.

The acrylic latex polymer also contains sufficient polymerized monoethylenically unsaturated acid monomers. Typically useful monoethylenically unsaturated acids are methacrylic acid, acrylic acid, itaconic acid, styrene sulfonic acid and salts thereof. Usually, these unsaturated acids are used in an amount of about 0.5-10% by weight, based on the weight of the polymer.

The remaining constituents of the acrylic latex polymer are polymerized alkyl acrylates and/or

methacrylates preferably, having about 1-12 carbon atoms in the alkyl group. These constituents are blended to provide the desired polymer glass transition temperature. Also, up to about 30% by weight of styrene can be used to form the acrylic latex polymer.

The following are particularly useful acrylic latex polymers:

an acrylic polymer containing about 30-40% by weight methyl methacrylate, 10-20% by weight styrene, 35-45% by weight 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight hydroxyethyl acrylate and 1-5% by weight methacrylic acid;

an acrylic polymer containing about 25-35% by weight methyl methacrylate, 10-20% by weight styrene, 45-55% by weight 2-ethylhexyl acrylate, 1-6% by weight methylol methacrylamide, 1-5% by weight hydroxyethyl acrylate and 1-5% by weight methacrylic acid;

an acrylic graft copolymer of stage I of 10-30% by weight of methyl methacrylate, 1-5% by weight methylol methacrylamide, 70-89% by weight butyl acrylate grafted to stage II of 70-80% by weight of butyl acrylate, 5-15% by weight methylol methacrylamide, 5-15% by weight hydroxyethyl acrylate and 5-9% by weight methacrylic acid; and

a three stage acrylic graft copolymer polymer, wherein stage I and stage II each comprise methyl methacrylate and butyl acrylate, and stage III comprises methyl methacrylate, butyl acrylate and methylol methacrylamide.

The acrylic hydrosol polymer is formed by conventional solution polymerization by adding a mixture of monomers, solvent and polymerization catalyst to a conventional polymerization reactor and heating the constituents in the reactor to reflux temperature of the

solvent of about 60-120°C for about 15 minutes to 8 hours to form a polymer solution. Then water and ammonia or an amine are added to the polymer solution to form a hydrosol. The size of the polymeric particles of the hydrosol is less than 0.30 microns. The resulting polymer has a hydroxyl no. of 2-100, a glass transition temperature of -40 to +45°C and a weight average molecular weight of about 5,000 - 75,000.

Typical catalysts used to form the hydrosol polymer, benzoyl peroxide, hydrogen peroxide and other peroxy compounds used for acrylic free radical polymerization, tertiary butylperacetate, tertiary butyl peroctoate, azoisobutyronitrile and other "Vazo" catalysts that are used for acrylic free radical polymerization.

Typically useful solvents are alcohols such as n-propanol, ethanol, methanol, n-butanol, mono and dialkyl ethers of ethylene glycol, such as ethylene glycol monobutyl ether, ethylene glycol monobutyl ether acetate, ethylene glycol dibutyl ether and the like.

The acrylic hydrosol polymer contains about 1-30% by weight of polymerized methylol methacrylamide, methylol acrylamide or any mixtures thereof.

The acrylic hydrosol polymer preferably contains sufficient polymerized hydroxy alkyl methacrylate or acrylate having 2-4 carbon atoms in the alkyl group to provide the polymer with a hydroxyl no. of 2-100. Usually, about 0.5-10% by weight of hydroxy alkyl acrylate or methacrylate is used. Typically useful monomers are shown above. Other useful polymerizable constituents are reaction products of an alkyl methacrylate or acrylate and a lactone such as "Tone" 100 described above.

The acrylic hydrosol polymer also contains sufficient polymerized monoethylenically unsaturated

acid monomers. Typically useful monoethylenically unsaturated acids are methacrylic acid, acrylic acid, itaconic acid, styrene sulfonic acid and salts thereof. Usually, these unsaturated acids are used in an amount  
5 of about 0.5-10% by weight, based on the weight of the polymer.

The remaining constituents of the acrylic hydrosol polymer are polymerized alkyl acrylates and/or methacrylates preferably having about 1-12 carbon atoms  
10 in the alkyl group. These constituents are blended to provide the desired polymer glass transition temperature. Typically useful monomers are described above. Also, up to about 40% by weight of styrene can be used to form the hydrosol polymer.

15 The following are particularly useful acrylic hydrosol polymers:

an acrylic polymer containing about 25-50% by weight methyl methacrylate (MMA), 10-30% by weight styrene (S), 25-50% by weight 2-ethylhexyl acrylate  
20 (2-EHA) or 2-ethylhexyl methacrylate (2-EHMA), 2-10% by weight methylol methacrylamide (MOLMAM), 2-10% by weight hydroxyethyl acrylate (HEA) and 1-6% by weight methacrylic acid (MMA);

The hydrosol polymer can contain about 0.1-2%  
25 by weight of polymerized surface active monomers such as SAM 185 having an HLB value of 6.9, SAM 186 having an HLB value of 9.9 and SAM 187 having an HLB value 14.0. These monomers are supplied by PPG-MAZER, Chemicals Group Technical Center, PPG Industries, Inc., 440  
30 College Park Drive, Monroeville, PA. These monomers are characterized by the structure:

Reactive Group (allyl) - hydrophobe -  
(OCH<sub>2</sub>)<sub>n</sub>CH<sub>2</sub>-CH=CH<sub>2</sub>OH. where n is 1 - 100.

Another useful surface active monomer is the sodium salt of allyl dodecyl sulfosuccinate. These monomers are supplied by Henkel Chemical Corp., Ambler, PA under the trade name TREM LF-40. Mixtures of any of the above surface active monomers can be used.

About 0.1-5% by weight, based on the weight of the coating composition, of carbodiimides or polyfunctional aziridines can be added to the waterborne coating composition which provide for additional crosslinking sites. These compounds can be added to the acrylic latex or acrylic hydrosol or to the resulting coating composition. Typically useful carbodiimides have the following structural formula:



where  $R_1$  and  $R_2$  are alkyl groups containing 1-8 carbon atoms. One particularly useful carbodiimide is "UCARLNC" Crosslinker XL-25SE made by Union Carbide Corporation.

Useful polyfunctional aziridines include trimethylolpropane-tris-[B-(N-aziridiny)propionate] and pentaerythritol-tris-[B-(N-aziridiny)propionate].

Pigments are used in the waterborne basecoating composition generally in a pigment to binder ratio of about 1:100 to 200:100. Typical pigments that can be used are metallic oxides such as titanium dioxide, zinc oxide, iron oxides of various colors, carbon black, filler pigments such as talc, china clay, barytes, carbonates, silicates, and a wide variety of organic colored pigments such as quinacridones, copper phthalocyanines, perylenes, azo pigments, indanthrone blues, carbazoles such as carbazole violet, isoindolinones, isoindolones, thioindigo reds, benzimidazolinones and the like.

When the coating contains metallic pigments, agents which inhibit the reaction of the pigments with water may be added. Typical inhibitors are phosphated organic materials such as "Vircopet" 40 available from Mobil Chemical Co.

The waterborne basecoating composition can contain about 0.01-2% by weight, based on the weight of the binder, of any of the aforementioned ultraviolet light stabilizers which includes ultraviolet light absorbers, screeners and quenchers that are used in the clear coat.

Thickeners and rheology control agents can be added to the waterborne basecoating composition in amounts of about 0.5-10% by weight of the coating composition to provide the desired spray viscosity. Typically, acrylic polymers such as polyacrylic acid, clays such as "Bentones", cellulosics, urethanes, silicas, associative thickeners such as "Rheolate" 255 or compatible mixtures of any of the above can be added.

Both the clear coating composition and the basecoating composition can be applied to plastic or metal substrates by conventional techniques such as spraying, electrostatic spraying, dipping, brushing, flowcoating and the like. The preferred method is spraying.

In applying the clear coat/basecoat, a basecoat of the waterborne pigmented coating composition is applied to a substrate which may be primed with a conventional primer or primed and sealed by one of the aforementioned coating methods. Spraying is usually used. The coating is applied to a dry film thickness of about 0.1-3.0 mils. The basecoat usually is dried but not fully cured either at ambient temperatures for about 5-30 minutes or at elevated temperatures for shorter period of time. A clear coating is then applied by one



of the aforementioned methods, usually spraying or electrostatic spraying is used. About 1-5 mils (dry film thickness) of the clear layer is applied. The clear coat/basecoat is then cured at ambient temperatures.

5           The following example illustrates the invention. All parts and percentages are on a weight basis unless otherwise indicated.

EXAMPLE 1

10           A clear solvent based coating composition is formed by preparing an acrylic polyol then blending the acrylic polyol with a polyisocyanate and other constituents.

15           The acrylic polyol is prepared by charging the following constituents into a polymerization reactor equipped with an addition funnel, a reflux condenser, a heating source and a thermometer:

	<u>Parts by Weight</u>
<u>Portion 1</u>	
Methyl amyl ketone	494.20
20 <u>Portion 2</u>	
Iso-butyl methacrylate	608.17
2-ethylhexyl methacrylate	790.74
2-hydroxyethyl methacrylate	429.89
<u>Portion 3</u>	
25 Methyl amyl ketone	196.80
t-butyl peracetate	88.20
<u>Portion 4</u>	
t-butyl peracetate	22.00
Methyl amyl ketone	<u>49.20</u>
30           Total	2678.63

Portion 1 is charged into the reactor and heated to its reflux temperature of about 150-155°C. Portion 2 is premixed and added to the reactor at a uniform rate over a 150 minute period with constant  
35 agitation and maintaining the above reflux temperature.

15

Portion 3 is charged into the reactor over 165 minute period along with Portion 2 and the reaction mixture was held at its reflux temperature for an additional hour. Portion 4 was added over a 30 minute period and the temperature was held at about 130°C .

The resulting acrylic polyol solution has a solids content of 68%, A Gardner-Holdt viscosity of T measured at 25°C and the acrylic polyol has an acid no. of 3.6 and a weight average molecular weight of about 5,000 determined by gel permeation chromatography using polymethylmethacrylate as the standard.

A clear coating composition was prepared by thoroughly mixing together the following constituents:

Parts by Weight

Portion 1

Acrylic polyol solution (prepared above) 101.44

Tinuvin®1130 UV light absorber 3.52  
(reaction product of

β-3-(2H-benzotriazol (2-yl)-4-hydroxy-5-tert-butyl phenyl propionic acid methyl ester and propylene glycol 300 from Ciba-Geigy)

CGL123 HALS antioxidant (hindered amine from Ciba-Geigy) 2.34

Resiflow S flow control agent (from Monsanto) 0.88

Dibutyl tin dilaurate solution (10% solids in xylene) 7.62

Portion 2

Cythane®3160 59.90  
(adduct of 3 moles of tetramethylxylidene diisocyanate and 1 mole of trimethylol propan )

35

Portion 4

Solvent blend (70/30 PM acetate/hexyl acetate) 8.41  
Methyl ethyl ketone 8.45

Total 200.00

5

The resulting coating composition had a solids content of 58.99%, VOC 3.34 lb/gal., viscosity (No. 2 Zahn cup) 38 sec., viscosity after 4 hours at room temperature 95 seconds, time to tack free state after application to a substrate 2.25 hours.

10

A Primer Composition was prepared as follows:

Millbase preparation:

Parts by Weight

15 Triton X-100 (nonionic surfactant - nonyl phenoxy ethyleneoxy ethanol 10 moles EO) 1.38  
Deionized water 39.62  
Aqueous ammonium hydroxide solution (29% solution) 0.39  
"Tamol" 901 (made by Rohm & Hass, ammonium salt of acrylic copolymer dispersant) 1.48  
20 Talc 34.25  
Aluminum silicate pigment 17.13  
Carbon black pigment 0.04  
Titanium dioxide pigment 5.71

Total 100.00

25

The above constituents are charged into a sand mill and ground to form a uniform dispersion.

The following ingredients were added in order with mixing to form a primer:

30

Parts by Weight

Pine oil 7.20  
Latex A<sup>1</sup> 216.22  
Acrylic Hydrosol<sup>2</sup> 100.00

35

17

Blend 1 (deioniz d water 23.57, "Butyl	14.40
Cellosolve" 3.58, aqueous ammonium	
hydroxide solution 1.57 and "Acrysol"	
TT615-Rohm & Hass acrylic acid	
5 copolymer thickner 4.10)	
Mill base (prepared above)	<u>315.07</u>
Total	652.89

Latex A<sup>1</sup> - acrylic polymer dispersed in water and having  
 10 weight solids of 38.4%, volume solids 35.7%, pH of 8.5,  
 the acylic polymer contains methyl methacrylate/styrene/  
 n-methylol methacrylamide/2-hydroxy ethyl acrylate/  
 methacrylic acid in a weight ratio of 27/15/49/3/3/3 and  
 a weight average molecular weight of 500,000-1,250,000  
 15 and is neutralized with ammonium hydroxide and has a  
 particle size of about 0.094 microns.

Acrylic Hydrosol 2 - acrylic polymer fine dispersion in  
 water having a polymer solids content of 20%, the  
 acrylic polymer contains methyl methacrylate/styrene/  
 20 n-methylol methacrylamide/2-hydroxy ethy acrylate/  
 methacrylic acid in a weight ratio of 31/22/34/3/3 and  
 has a weight average molecular weight of about 40,000  
 and is neutralized with ammonium hydroxide.

The resulting primer composition has a solids  
 25 content of about 42%, and a pigment/binder ratio of  
 180:100.

The primer was sprayed onto cold-rolled steel  
 panels and dried at ambient temperatures. The primer  
 had a dry film thickness of about 1.8-2.2 mils.

30 A silver basecoating composition was prepared  
 by mixing together the following constituents in the  
 order shown and and thoroughly blending these  
 constituents:

35

18

		<u>Parts by Weight</u>
	"Butyl Cellosolve"	13.42
	Inhibitor solution	10.68
	(phosphated organic inhibitor)	
5	Aluminum flake paste	23.04
	(65% solids in mineral spirits)	
	"Butyl Cellosolve"	14.96
	Blend 1 (described above)	30.00
	Deionized water	198.00
10	Latex A <sup>1</sup> (described above)	193.00
	Acrylic Hydrosol <sup>2</sup> (described above)	<u>99.50</u>
	Total	582.60

15 The basecoat was sprayed onto the above prepared primed cold-rolled steel panels and flash dried and the clear coating prepared above was spray applied and both of the coatings were dried at ambient temperatures for about 2.25 hours to form a tack free finish having a high gloss and a very good appearance.

20 minutes. The resulting basecoat had a dry film thickness of about 0.6 - 0.8 mils. and the clear coat had a dry film thickness of about 1.8-2.1 mils.

The finish on the panels had the following properties:

25 Hardness (Persoz) after 1 day - 96  
Hardness (Persoz) after 3 days - 170  
Hardness (Persoz) after 7 days - 201

The above data shows that additional cure of the finish occurred at ambient temperatures to improve hardness

30 properties of the finish.

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CLAIMS

What is claimed is:

1. In a process for forming multiple coats of finishes on a substrate comprising sequential steps of
  - 5 (a) applying to the substrate a layer of a color basecoat composition comprising a waterborne coating composition of a film forming binder of an acrylic polymer latex and containing pigment in a pigment to binder weight ratio of about 1:100 to 150:100 dispersed
  - 10 in an aqueous medium; (b) applying to the layer of color basecoat composition before the base coat composition is fully cured a clear coat composition of an acrylic polymer having crosslinkable groups and a crosslinking agent in a volatile organic solvent and (c) subsequently
  - 15 simultaneously curing the basecoat composition and the clear coat composition; the improvement used therewith comprises the clear coating composition comprising about 40-80% by weight, based on the weight of the coating composition, of binder in volatile organic solvent;
  - 20 wherein the binder consists essentially of about 40-95% by weight, based on the weight of the binder, of an acrylic polymer consisting essentially of polymerized monomers of at least two alkyl methacrylates having 2-12
  - 25 carbon atoms in the alkyl group and a hydroxy alkyl methacrylate having 2-4 carbon atoms in the alkyl group and having a weight average molecular weight of about 3,000-10,000 and a glass transition temperature of about
  - 30 -20 to +50°C;
  - and
  - 5-60% by weight, based on the weight of the binder of an organic polyisocyanate crosslinking agent;

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wherein the clear coat when cured has a water vapor permeability value of about 1400-3200.

2. The process of claim 1 in which the  
5 organic polyisocyanate of the clear layer partially penetrates into the color base coat and crosslinks the base coat and bonds the clear coat to the based coat.

3. The process of claim 2 in which the clear  
10 coat contains about 0.1-10% by weight, based on the weight of the binder of the clear coat, of antioxidants and ultraviolet light absorbers.

4. The process of claim 3 in which the  
15 organic polyisocyanate is an isocyanate terminated adduct of an organic diisocyanate and a polyol.

5. The process of claim 4 in which the  
20 organic diisocyanate is an aromatic diisocyanate and the polyol is a trimethylol alkane.

6. The process of claim 5 in which the  
organic diisocyanate is tetramethyl xylidene diisocyanate and the polyol is trimethylol propane.

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7. The process of claim 2 in which the acrylic polymer consists essentially of 70-90% by weight of at least two alkyl methacrylates and 10-30% by weight of hydroxy alkyl methacrylate.

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8. The process of claim 7 in which the acrylic polymer contains about 0.5-40% by weight polymerized styrene.

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9. The process of claim 7 in which the acrylic polymer consists essentially of about 20-40% by weight of isobutyl methacrylate, 35-65% by weight of 2-ethylhexyl methacrylate and 15-30% by weight of 2-hydroxyethyl methacrylate.

10. The process of claim 1 in which the clear coat contains about 0.1-10% by weight, based on the weight of the binder, of an alkyl metal catalyst.

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11. The process of claim 10 in which the catalyst is dibutyl tin dilaurate.

12. The process of claim 2 in which the acrylic polymer of the clear coat consists essentially of 20-40% by weight of isobutyl methacrylate, 35-65% by weight of 2-ethylhexyl methacrylate and 15-30% by weight of 2-hydroxyethyl methacrylate and the organic polyisocyanate crosslinking agent consists essentially of an isocyanate terminated adduct of tetramethyl xylidene diisocyanate and trimethylol propane.

13. A substrate having multiple coats of finishes thereon comprising a layer of a color basecoat composition comprising a cured layer of a waterborne coating composition of a film forming binder of an acrylic polymer latex and containing pigment in a pigment to binder weight ratio of about 1:100 to 150:100; a clear coat composition of an acrylic polymer having crosslinkable groups and a crosslinking agent in adherence to the color base coat; wherein the basecoat and the clear coat being simultaneously cured and the crosslinking agent of the clear coat partially penetrates the basecoat to bond the clear coat to the basecoat;



wherein the clear coat is formed from a coating composition comprising about 40-80% by weight, based on the weight of the coating composition of binder in volatile organic solvent; wherein the binder consists  
5 essentially of about

40-95% by weight, based on the weight of the binder, of an acrylic polymer consisting essentially of polymerized monomers of at least two alkyl methacrylates having 2-12  
10 carbon atoms in the alkyl group, a hydroxy alkyl methacrylate having 2-4 carbon atoms in the alkyl group and the polymer having a weight average molecular weight of about 3,000-10,000 and a glass transition  
15 temperature of about -20 to +50°C;  
and

5-60% by weight, based on the weight of the binder of an organic polyisocyanate crosslinking agent;  
20 wherein the clear coat when cured has a water vapor permeability value of about 1400-3200.

14. The substrate of claim 13 in which the clear coat contains about 0.1-10% by weight, based on  
25 the weight of the binder of the clear coat, of antioxidants and ultraviolet light absorbers.

15. The substrate of claim 13 in which the organic polyisocyanate is an isocyanate terminated  
30 adduct of an organic diisocyanate and a polyol.

16. The substrate of claim 15 in which the organic diisocyanate is an aromatic diisocyanate and the polyol is a trimethylol alkane.

17. The substrate of claim 15 in which the organic diisocyanate is tetramethyl xylidene diisocyanate and the polyol is trimethylol propane.

5           18. The substrate of claim 13 in which the acrylic polymer consists essentially of 70-90% by weight of at least two alkyl methacrylates and 10-30% by weight of hydroxy alkyl methacrylate.

10           19. The substrate of claim 18 in which the acrylic polymer consist essentially of about 20-40% by weight of isobutyl methacrylate, 35-65% by weight of 2-ethylhexyl methacrylate and 15-30% by weight of 2-hydroxyethyl methacrylate.

15           20. The substrate of claim 13 in which the clear coat contains about 0.1-10% by weight, based on the weight of the binder, of an alkyl metal catalyst.

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## INTERNATIONAL SEARCH REPORT

PCT/US 92/04194

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08G18/62; B05D1/36; C09D133/14

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System

Classification Symbols

Int.Cl. 5

C08G ; B05D ; C09D

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	DE,A,3 918 968 (KANSAI PAINT CO.) 14 December 1989  see claims 1-4 see page 4, line 28 - line 55 see page 7, line 28 - line 68 see page 8, line 30 - line 52 ---	1,3-5, 10,11, 13-16,20
X	GB,A,2 171 030 (KANSAI PAINT CO.) 20 August 1986 see claims 1,3-5 see page 4, line 15 - line 46 see page 5, line 2 - line 59 ---	1,2,13
A	EP,A,0 375 823 (BASF CORP.) 4 July 1990 see claims 3,4 see page 2, line 30 - line 55 ---	1
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<sup>10</sup> Special categories of cited documents : <sup>10</sup><sup>10</sup> "A" document defining the general state of the art which is not considered to be of particular relevance<sup>10</sup> "E" earlier document but published on or after the international filing date<sup>10</sup> "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<sup>10</sup> "O" document referring to an oral disclosure, use, exhibition or other means<sup>10</sup> "P" document published prior to the international filing date but later than the priority date claimed<sup>10</sup> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<sup>10</sup> "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<sup>10</sup> "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<sup>10</sup> "A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

08 SEPTEMBER 1992

Date of Mailing of this International Search Report

16. 09. 92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

VAN PUymbROECK M. A.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	GB,A,2 109 385 (NIPPON PAINT CO.) 2 June 1983 see claims 1,3,5,6  ---	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9204194  
SA 60902

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 08/09/92

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		DE-A,C 3600425	31-07-86
		US-A- 4759961	26-07-88
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GB-A-2109385	02-06-83	JP-A- 58076469	09-05-83
		DE-A- 3240043	05-05-83
		FR-A,B 2515674	06-05-83
		US-A- 4463038	31-07-84